Introducing the Agilent Pesticide & Environmental Pollutant GC/MS/MS Analyzer 2.0

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EPRW 2012

GC/MS Multi-Residue Pesticide Analysis

5975C SQ

Scan, SIM, SIM / Scan

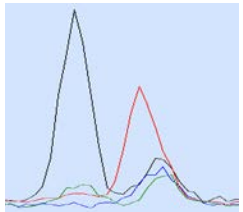
7000B QQQ

MRM

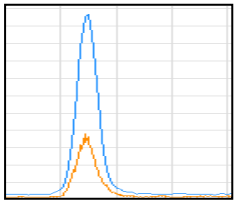
GC/MS SIM vs. GC/QQQ; Dieldrin at 10 ppb

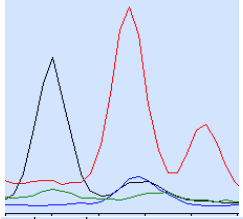
***GC/SIM m/z* 263, 265, 277,279**

GC/QQQ MRM 263 →191 & 263→193

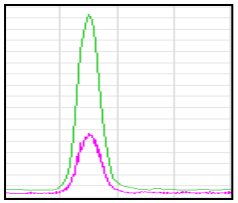


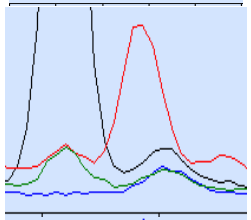
Apple



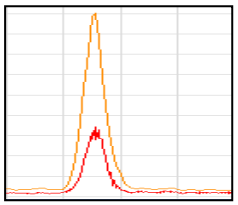


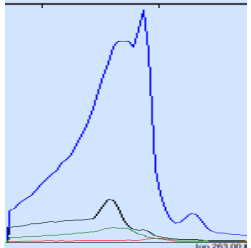
Cabbage



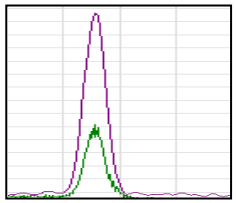


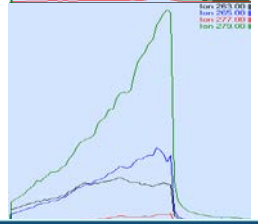
Ginseng



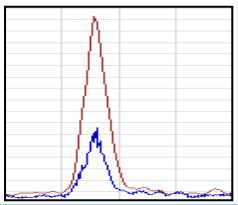


Orange





Spinach



The Analyzer Concept -- Enable customer to produce high performance result from DAY ONE

Std. HW, SW

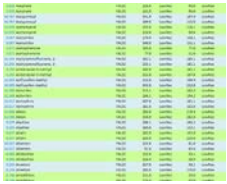
w/o Analyzer

App. optimized consumables

Factory setup and chemically tested Analyzer

System with application setup

Familiarization



Application report

Fast Track Analyzer

Factory Setup & Checkout

CE Specialist Analyzer I&F

Consulting or Field Sol.

Aftermarket

Individual Components produced	Individual Components Tested (OFN)	System assembled	App. method developed on cust. system	System checkout on App. mix	Run 1st customer sample	customization or optimization method	On-going maintains/service
Box Selling		CE Setup; Boxes I&F	Customer on Their Own				Aftermarket

The Advantages of P&EP GC/MS/MS Analyzer 2.0

Retention Time Locking	• **Allow simple and rapid system set-up** and easy data comparison between ECD, MSD, MS/MS…
Multimode inlet (MMI)	• **Large-volume injection enhances trace-level detection** – inlet adds flexibility by including standard, cold split/splitless, and solvent vent (LVI) capabilities
Capillary Flow Technology (CFT) and backflush	• **Improve uptime** - shorter analysis time, more consistent retention times and spectra, longer column life, and less frequent source cleaning
Pre-configured and factory set-up / tested	• **Factory set-up and checked out on pesticide mixture** ready to generate results on Day One

Building Customized Pesticide Multi-Residue MRM Methods

Most laboratories have their own tailor-made lists of target analytes, how can they easily and quickly create customized GC-MS/MS MRM methods?

5975C SQ
Scan, SIM, SIM / Scan

7000B QQQ
MRM

G9250AA

Comprehensive MS/MS MRM Database

New!

- **Comprehensive and Flexible Optimized MRM database** for 1000+ compounds, ready to use and customer can create customized method in minutes !

The Most Comprehensive and Flexible MRM database

❖**1000+ Pesticides & Environmental Pollutants**

Compound Classification	Total Number
Pesticides (fungicides, herbicides, insecticides, rodenticides and others)	675
Breakdown Products	42
Deuterated Compounds	6
Polybrominated Diphenyl Ether (PBDE)	4
Polybrominated Biphenyl (PBB)	1
Polychlorinated Biphenyl (PCB)	209
Polycyclic Aromatic Hydrocarbon (PAH)	26
Phthalates	17
Additional Semi-volatile Pollutants	94

❖**Average of 8 MRM transitions for each compound (Total > 8500)**

-- provides alternatives to **avoid matrix interferences**

-- includes relative intensities for all transitions

We collected $70,000 worth of chemicals and made >3500 runs, so customers don't have to!

The Most Comprehensive and Flexible MRM database

- **Each compound has 13 characteristics**

  -- allows **easy searching and filtering** for method customization

  - ✓ 2 formats of CAS number (with or without dashes)
  - ✓ 2 classifications based on compound usage and functional group
  - ✓ Averaged and mono-isotope molecular weights
  - ✓ Molecular formula
  - ✓ Compound name in 3 languages (English, Chinese, Japanese)
  - ✓ Relative intensity of each transition (easy to filter out all intensities > 50%)
  - ✓ Transitions in descending order within a compound (easy to filter out top 1, 3, or 5 etc.)
  - ✓ User specified field (tagging compounds to regulatory or internal methodologies)

The Most Comprehensive and Flexible MRM database

❖ **Tools and macros for easy custom method creation**

-- two ways to build an MRM method, based on **their** compound list, in **5 minutes**

- ✓ Use Compounds List Assistant (from MassHunter) for time segment overlap, or
- ✓ Use Excel-based macro to adjust time segments and optimize dwell times

❖**Retention times (RT) and indexes (RI) for three GC methods included**

- ✓ **Fast method**: 20-min run, constant flow (CF), mid-column back flush
- ✓ **Full screening method**: 40-min run, constant flow (CF), mid-column back flush
- ✓ **Flexible method**: 40-min run, constant pressure (CP), post-column back flush

The Most Comprehensive and Flexible MRM database

- **Three easy learning videos supplied with database**
  - ✓ Overview of the Database
  - ✓ How to build your custom acquisition method
  - ✓ How to add compounds to the Database

Access videos on Agilent.com website
https://www.chem.agilent.com/en-US/Products/Instruments/ms/gc-ms/systems/7000triplequadrupolegcms/pages/default.aspx

Or on YouTube Broadcast Yourself

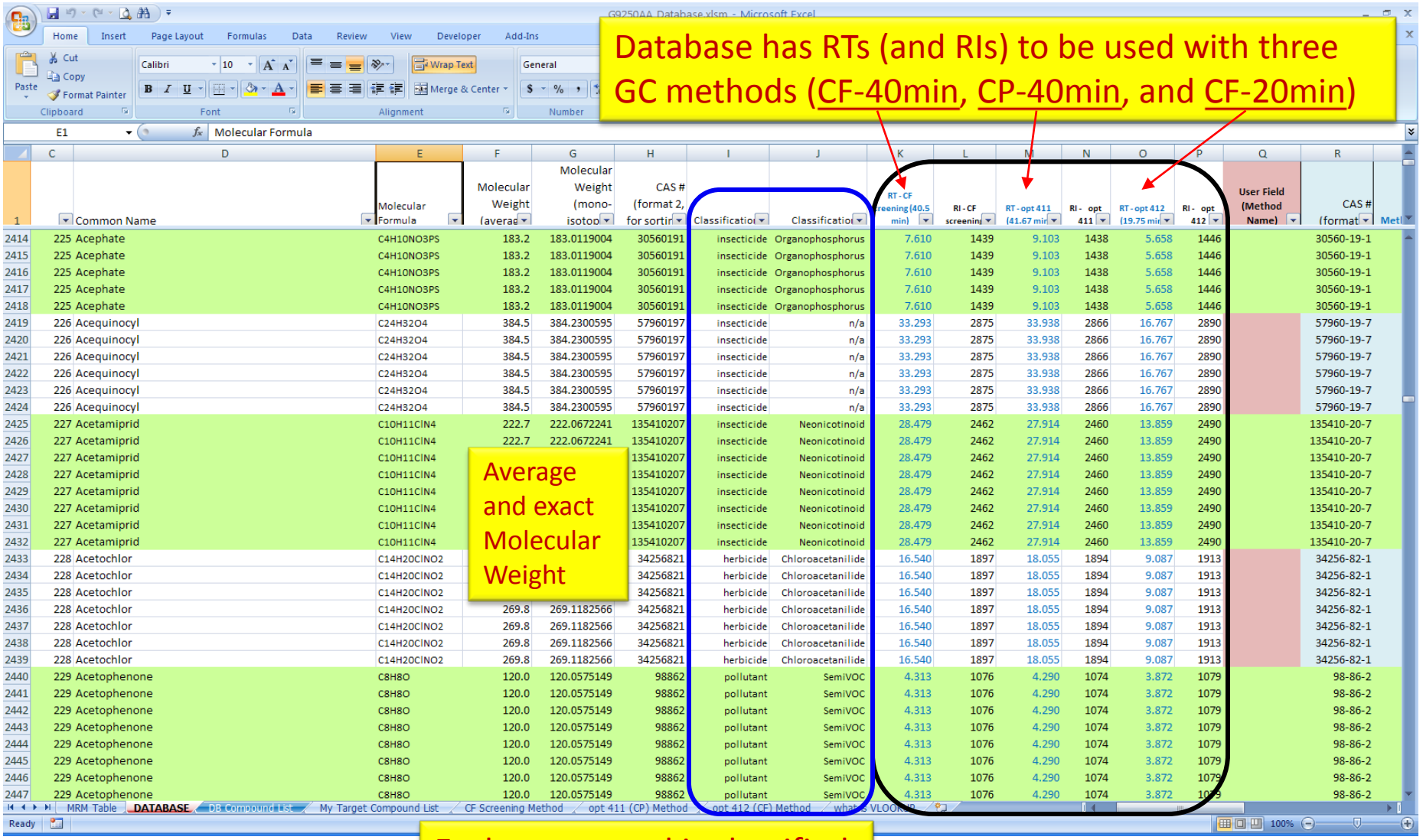
http://www.youtube.com/watch?v=-q7ytZDtRAs

http://www.youtube.com/watch?v=ayZjwcRM3y0

http://www.youtube.com/watch?v=51ltSDxF0Us

G9250AA – Pesticide / Environmental Pollutant MRM Database

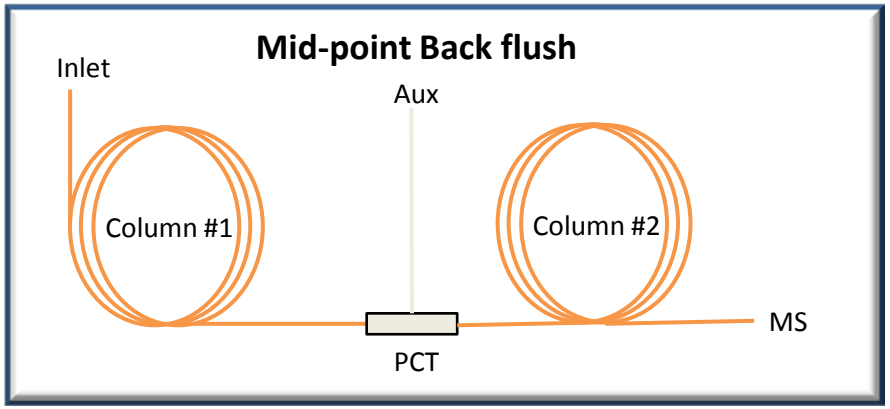
The Flexibility: Multi-transitions; classifications; 3 RTs and RIs

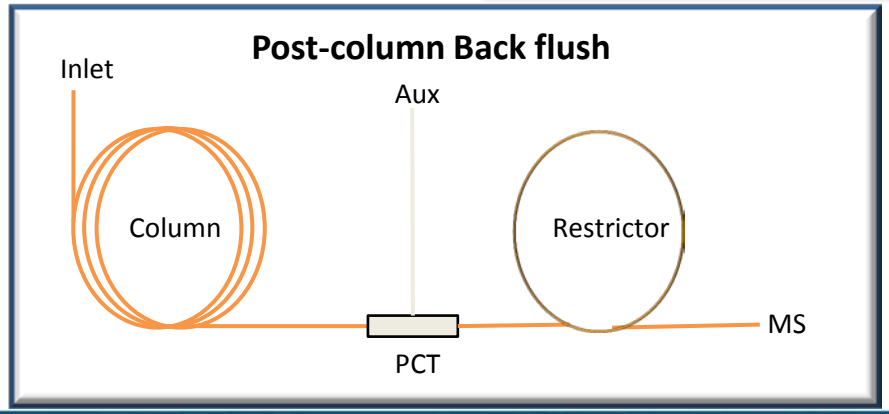


	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1		Common Name	Molecular Formula	Molecular Weight (averag	Molecular Weight (mono-isotop	CAS # (format 2, for sortir	Classificatio	Classificatio	RT - CF reening (40.5 min)	RI - CF screenin	RT - opt 411 (41.67 mir	RI - opt 411	RT - opt 412 (19.75 mir	RI - opt 412	User Field (Method Name)	CAS # (format
2414	225	Acephate	C4H10NO3PS	183.2	183.0119004	30560191	insecticide	Organophosphorus	7.610	1439	9.103	1438	5.658	1446		30560-19-1
2415	225	Acephate	C4H10NO3PS	183.2	183.0119004	30560191	insecticide	Organophosphorus	7.610	1439	9.103	1438	5.658	1446		30560-19-1
2416	225	Acephate	C4H10NO3PS	183.2	183.0119004	30560191	insecticide	Organophosphorus	7.610	1439	9.103	1438	5.658	1446		30560-19-1
2417	225	Acephate	C4H10NO3PS	183.2	183.0119004	30560191	insecticide	Organophosphorus	7.610	1439	9.103	1438	5.658	1446		30560-19-1
2418	225	Acephate	C4H10NO3PS	183.2	183.0119004	30560191	insecticide	Organophosphorus	7.610	1439	9.103	1438	5.658	1446		30560-19-1
2419	226	Acequinocyl	C24H32O4	384.5	384.2300595	57960197	insecticide	n/a	33.293	2875	33.938	2866	16.767	2890		57960-19-7
2420	226	Acequinocyl	C24H32O4	384.5	384.2300595	57960197	insecticide	n/a	33.293	2875	33.938	2866	16.767	2890		57960-19-7
2421	226	Acequinocyl	C24H32O4	384.5	384.2300595	57960197	insecticide	n/a	33.293	2875	33.938	2866	16.767	2890		57960-19-7
2422	226	Acequinocyl	C24H32O4	384.5	384.2300595	57960197	insecticide	n/a	33.293	2875	33.938	2866	16.767	2890		57960-19-7
2423	226	Acequinocyl	C24H32O4	384.5	384.2300595	57960197	insecticide	n/a	33.293	2875	33.938	2866	16.767	2890		57960-19-7
2424	226	Acequinocyl	C24H32O4	384.5	384.2300595	57960197	insecticide	n/a	33.293	2875	33.938	2866	16.767	2890		57960-19-7
2425	227	Acetamiprid	C10H11ClN4	222.7	222.0672241	135410207	insecticide	Neonicotinoid	28.479	2462	27.914	2460	13.859	2490		135410-20-7
2426	227	Acetamiprid	C10H11ClN4	222.7	222.0672241	135410207	insecticide	Neonicotinoid	28.479	2462	27.914	2460	13.859	2490		135410-20-7
2427	227	Acetamiprid	C10H11ClN4			135410207	insecticide	Neonicotinoid	28.479	2462	27.914	2460	13.859	2490		135410-20-7
2428	227	Acetamiprid	C10H11ClN4			135410207	insecticide	Neonicotinoid	28.479	2462	27.914	2460	13.859	2490		135410-20-7
2429	227	Acetamiprid	C10H11ClN4			135410207	insecticide	Neonicotinoid	28.479	2462	27.914	2460	13.859	2490		135410-20-7
2430	227	Acetamiprid	C10H11ClN4			135410207	insecticide	Neonicotinoid	28.479	2462	27.914	2460	13.859	2490		135410-20-7
2431	227	Acetamiprid	C10H11ClN4			135410207	insecticide	Neonicotinoid	28.479	2462	27.914	2460	13.859	2490		135410-20-7
2432	227	Acetamiprid	C10H11ClN4			135410207	insecticide	Neonicotinoid	28.479	2462	27.914	2460	13.859	2490		135410-20-7
2433	228	Acetochlor	C14H20ClNO2			34256821	herbicide	Chloroacetanilide	16.540	1897	18.055	1894	9.087	1913		34256-82-1
2434	228	Acetochlor	C14H20ClNO2			34256821	herbicide	Chloroacetanilide	16.540	1897	18.055	1894	9.087	1913		34256-82-1
2435	228	Acetochlor	C14H20ClNO2			34256821	herbicide	Chloroacetanilide	16.540	1897	18.055	1894	9.087	1913		34256-82-1
2436	228	Acetochlor	C14H20ClNO2	269.8	269.1182566	34256821	herbicide	Chloroacetanilide	16.540	1897	18.055	1894	9.087	1913		34256-82-1
2437	228	Acetochlor	C14H20ClNO2	269.8	269.1182566	34256821	herbicide	Chloroacetanilide	16.540	1897	18.055	1894	9.087	1913		34256-82-1
2438	228	Acetochlor	C14H20ClNO2	269.8	269.1182566	34256821	herbicide	Chloroacetanilide	16.540	1897	18.055	1894	9.087	1913		34256-82-1
2439	228	Acetochlor	C14H20ClNO2	269.8	269.1182566	34256821	herbicide	Chloroacetanilide	16.540	1897	18.055	1894	9.087	1913		34256-82-1
2440	229	Acetophenone	C8H8O	120.0	120.0575149	98862	pollutant	SemiVOC	4.313	1076	4.290	1074	3.872	1079		98-86-2
2441	229	Acetophenone	C8H8O	120.0	120.0575149	98862	pollutant	SemiVOC	4.313	1076	4.290	1074	3.872	1079		98-86-2
2442	229	Acetophenone	C8H8O	120.0	120.0575149	98862	pollutant	SemiVOC	4.313	1076	4.290	1074	3.872	1079		98-86-2
2443	229	Acetophenone	C8H8O	120.0	120.0575149	98862	pollutant	SemiVOC	4.313	1076	4.290	1074	3.872	1079		98-86-2
2444	229	Acetophenone	C8H8O	120.0	120.0575149	98862	pollutant	SemiVOC	4.313	1076	4.290	1074	3.872	1079		98-86-2
2445	229	Acetophenone	C8H8O	120.0	120.0575149	98862	pollutant	SemiVOC	4.313	1076	4.290	1074	3.872	1079		98-86-2
2446	229	Acetophenone	C8H8O	120.0	120.0575149	98862	pollutant	SemiVOC	4.313	1076	4.290	1074	3.872	1079		98-86-2
2447	229	Acetophenone	C8H8O	120.0	120.0575149	98862	pollutant	SemiVOC	4.313	1076	4.290	1074	3.872	1079		98-86-2

Pre-Configured Analyzer RTL GC Methods

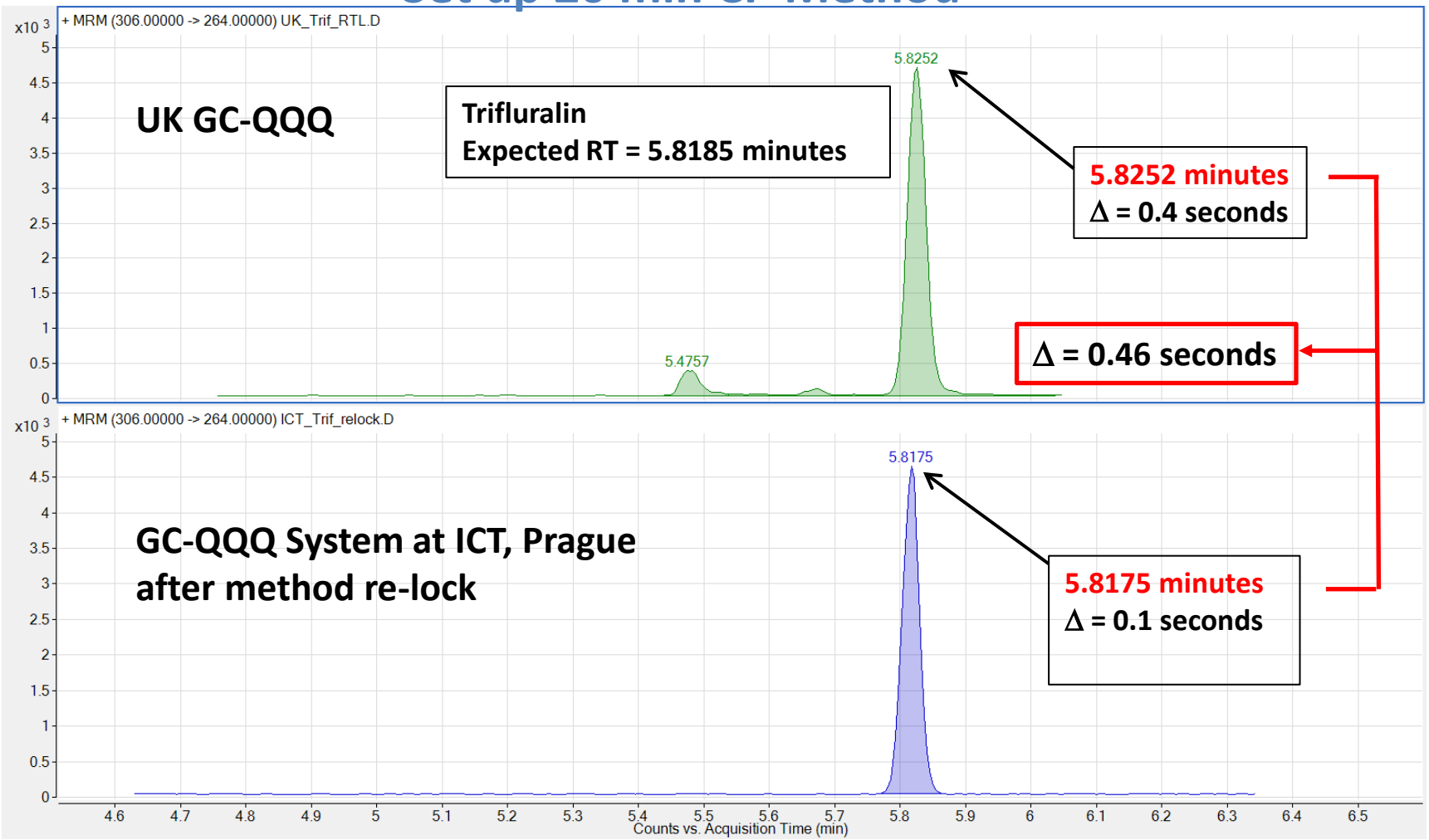
	40 Minute Constant Flow Method	20 Minute Constant Flow Method	40 Minute Constant Pressure Method	20 Minute Constant Pressure Method
Column(s)	2 x 15m	2 x 15m	1 x 30m	1 x 15m
Back flush type	Mid-point	Mid-point	Post-column	Post-column
# Targets	~300+	~200+	~300+	~200+





RTL GC/MS/MS Method

Set up 20 min CP Method



Load method, re-lock method on customer site and acquisition method is set-up

Case Study – UK Food Contract Lab

- Customer looking to move to GC-MS/MS (Mass Hunter) from several GC-MSD (ChemStation) systems for multi-residue pesticide analysis

- Build bespoke 178 compound MS/MS method
  - *Manually building MRM method took 2 days*
  - *now could use G9250AA MRM database and build the method in just a few minutes from a simple list of compound names & CAS numbers*

- Method :2x RTL Method, 15m HP-5MSUI Column, post column back flush (PCT)

- Green Bean and Mint extracts

GC-QQQ – 178 Target Analytes

Dichlorvos	Diazinon	Parathion ethyl	Methidathion	Carbophenothion	Tebufenpyrad
Dichlobenil	Phosphamidon I	Isobenzan	Bromophos-ethyl	Endosulfan sulfate	Fenazaquin
Biphenyl	BHC delta isomer	Chlorthal-dimethyl	Endosulfan (alpha isomer)	Quinoxyfen	Bifenox
Mevinphos	Paraoxon-methyl	Fenson	Pyrifenox II	Cyanofenphos	Tetradifon
Propham	Terbacil	Nitrothal-isopropyl	Chlordane, cis-		Phenothrin I
Methacrifos	Tefluthrin, cis-	Tetraconazole	Disulfoton sulfone	Propiconazole-II	Phenothrin II
Phenylphenol, o-	Etrimfos	Isodrin	Tetrachlorvinphos	DDT, o,p'-	Furathiocarb
Tecnazene	Chlorothalonil	Butralin	Paclobutrazol	DDT, p,p'-	Phosalone
Propachlor	Formothion	Pirimiphos-ethyl	Chlorfenson	Lenacil	Leptophos
Propoxur	Dichlofenthion	Cyprodinil	Hexaconazole	Propiconazole-I	Cyhalothrin I (lambda)
Diphenylamine	Metribuzin	Heptachlor epoxide	Prothiofos	Hexazinone	Benfuracarb
Demeton-S- methyl	Chlorpyrifos Methyl	Heptachlor exo-epoxide isomer B	Dieldrin	Nuarimol	Pyrazophos
Chlorpropham	Parathion methyl	Metazachlor	Profenofos	Tebuconazole	Acrinathrin
Dioxabenzofos	Spiroxamine I	Pendimethalin	DDE, p,p'-	Propargite	Dialifos
Benfluralin	Spiroxamine II	Penconazole	Fludioxonil	Piperonyl butoxide	Bitertanol I
Trifluralin	Vinclozolin	Tolylfluanid	Imazalil	Resmethrin I	Bitertanol II
Phorate	Heptachlor	Captan	Myclobutanil	Resmethrin II	Spirodiclofen
BHC alpha isomer	Tolclofos-methyl	Pyrifenox I	Endrin	Iprodione	Permethrin I
Hexachlorobenzene	Carbaryl	Chlozolinate	Kresoxim-methyl	Phosmet	Pyridaben
Dicloran	Paraoxon	Folpet	Cyproconazole	Pyridaphenthion	Permethrin II
Ethoxyquin		Isofenphos	Endosulfan (beta isomer)	Tetramethrin I	Prochloraz
BHC beta isomer	Prosulfocarb	Chlorfenvinphos	Chlorfenapyr	Bromopropylate	Cyfluthrin I-IV
Lindane	Fenitrothion	Quinalphos	Chlorobenzilate	EPN	Boscalid
Quintozene	Dichlofluanid	Fluazinam	Chlordecone	Fenoxycarb	Cypermethrin I-IV
Isocarbamide		Phenthoate	DDD, p,p'-	Carbosulfan	Fenvalerate I
Terbufos	Aldrin	Mecarbam	Oxadixyl	Dicofol, p,p'-	Fenvalerate II
Fonofos	Fenthion	Fipronil	Ethion	Bifenthrin	Fluvalinate-tau-I
Propetamphos	Diethofencarb	Furalaxyl	Tetrasul	Tetramethrin II	Indoxacarb
Propyzamide	Chlorthion	Procymidone	Mepronil	Methoxychlor	Deltamethrin
Pyrimethanil	Chlorpyrifos	Chlordane, trans-	Ofurace	Fenpropathrin	Famoxadone

MRM Acquisition Method built ‘by hand’ : 2 Day’s Work

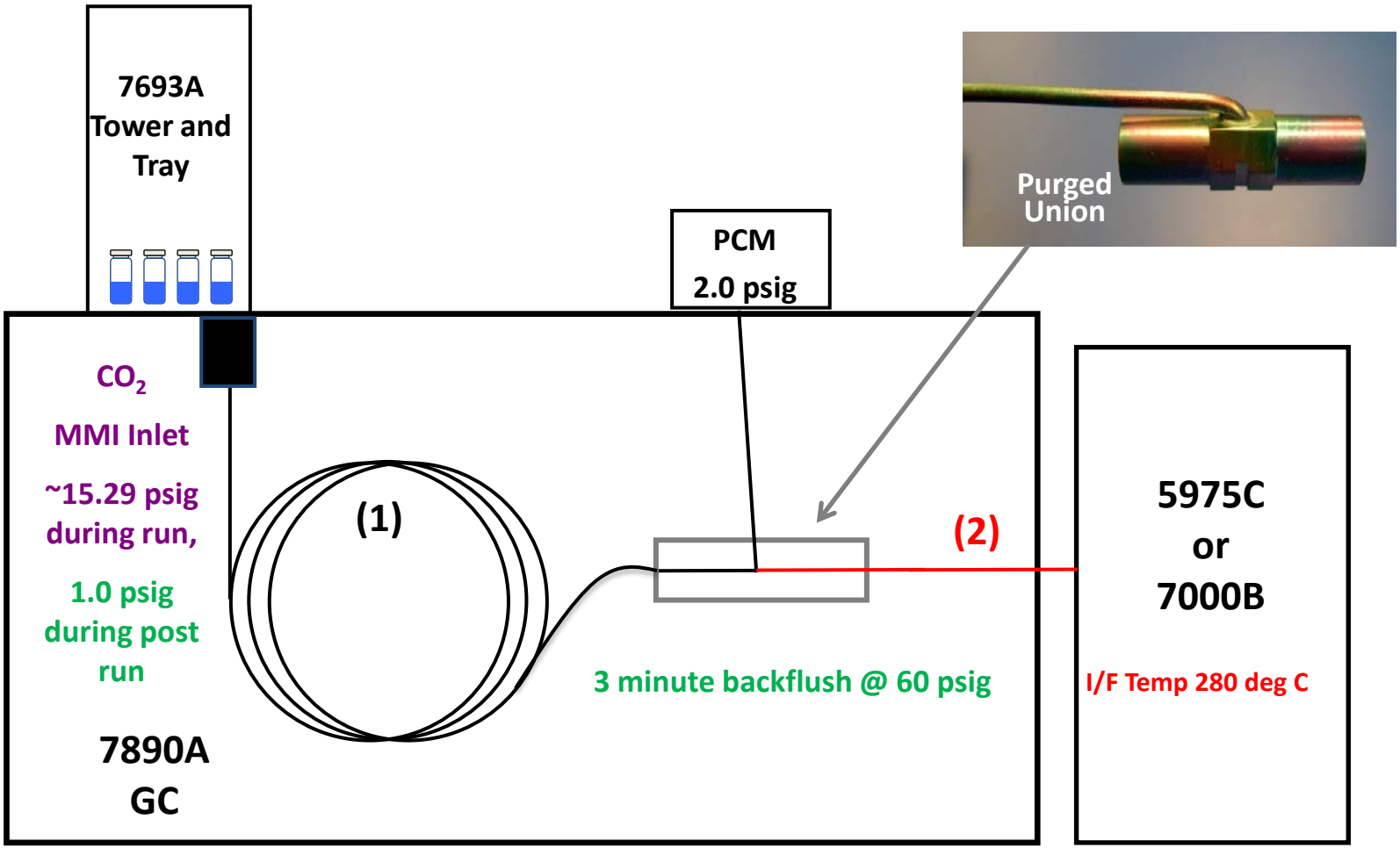
20 minute CP Pesticide Method

(1) Constant Pressure, Column 15 m X 0.25 mm id X 0.25 um HP-5MSUI

(2) Constant Pressure Restrictor 0.50 m X 0.15 mm id x 0.15um DB-5MSUI

MMI Liner
2mm ID
Dimpled
5190-2296

Or
UI Liner
4mm ID +
Glass Wool
5190-2293



Sequence Table – Order of Injections*

Inj #	Vial #	Type	Description
1	1	Blank	Blank
2	2	Blank	Blank
3	22	Blank	Lettuce extract
4	22	Blank	Lettuce extract
5	22	Blank	Lettuce extract
6	17	Calibration	Matrix Cal 10 ppb
7	18	Calibration	Matrix Cal 50 ppb
8	19	Calibration	Matrix Cal 100 ppb
9	20	Calibration	Matrix Cal 500 ppb
10	21	Blank	Blank
11	3	Sample	Spike low
12	4	Sample	Spike low
13	5	Sample	Spike high
14	6	Sample	Spike high
15	7	Blank	Blank
16	8	Blank	Blank
17	9	Sample	Spike low
18	10	Sample	Spike low
19	11	Sample	Spike high
20	12	Sample	Spike high
21	13	Sample	Green Bean extract
22	14	Sample	Green bean extract
23	15	Sample	Mint extract
24	16	Sample	Mint extract
25	17	Calibration	Matrix Cal 10 ppb
26	18	Calibration	Matrix Cal 50 ppb
27	19	Calibration	Matrix Cal 100 ppb
28	20	Calibration	Matrix Cal 500 ppb
29	21	Blank	Blank

Sequence ran 3 times on 3 consecutive days - no system maintenance performed between sequences

* Total time to run 29 injections = 13 hours 15 minutes

7000 QQQ Results – Green Bean & Mint Extracts

Quant Results – Extracts

	Batch Day 1	Batch Day 2	Batch Day 3	Batch Day 1	Batch Day 2	Batch Day 3
	Green Bean Extract	Green Bean Extract	Green Bean Extract	Mint Extract	Mint Extract	Mint Extract
	Mean ppb	Mean ppb	Mean ppb	Mean ppb	Mean ppb	Mean ppb
Biphenyl	3.1	2.6	2.7			
o-Phenyl phenol	0.4	0.4	0.4	0.6	0.6	0.6
Diphenylamine	0.6	0.6	0.6	1.3	1.2	1.2
Chloropropham	0.9	0.8	0.9			
Diazinon				1.1	1.1	1.0
Ethion	23.9	20.9	25.9			
Tebuconazole				408	412	417
Iprodione				16.0	14.3	15.6
λ-Cyhalothrin				362	349	350
Boscalid				8.0	8.0	7.0
Deltamethrin				75.0	80.6	62.5

Extracts also analyzed in full scan mode using 5975 MSD and Deconvolution Reporting Software - See *Additional Slides* section

INSTITUTE OF CHEMICAL TECHNOLOGY PRAGUE

Agilent Technologies

Determination of Multi-Pesticide Residues in Dried Tea Samples using an Optimized Extraction / Clean-up Regime and the Agilent 7000 Series Tandem Quadrupole GC/MS/MS System

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Institute of Chemical Technology
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in collaboration with

Chris Sandy
EMEA GC-MS Food Applications Chemist
Agilent Technologies UK

TEA : SAMPLE PREPARATION PROCEDURE

1. 2g dried tea leaves + 10mL water in 50 mL plastic centrifuge tube, shake 30 seconds, wait 30 minutes for matrix hydration

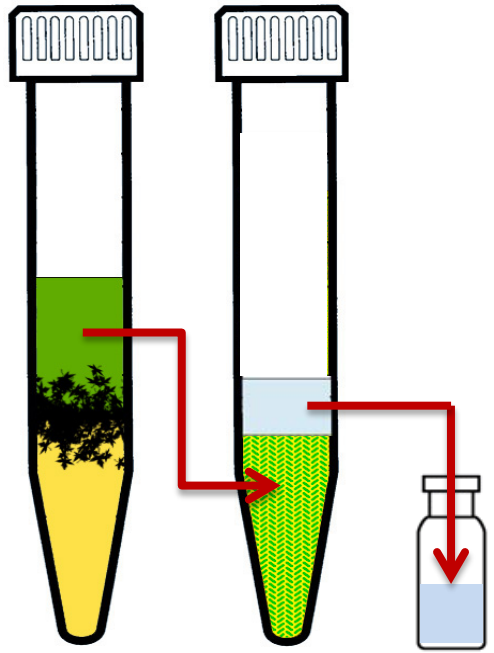
2. Add 10 mL acetonitrile; agitate 1 minute, Add 4g $MgSO_4$ + 1g NaCl; agitate 1 minute, add TPP (ISTD), centrifuge 5 minutes at 10,000 rpm

3. Take 1 mL acetonitrile layer in to a 15 mL plastic centrifuge tube, add 1 mL *n*-hexane and 5 mL 20% aqueous NaCl solution, agitate 1 minute

4. Centrifuge 1 minute at 10,000 rpm

5. Take part of *n*-hexane layer into 2 mL auto-sampler vial

Easily prepare 6 samples / hour



1-2 3-4 5

Acetonitrile Water Hexane

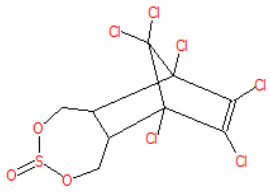
Acetonitrile / 20% Aq. NaCl

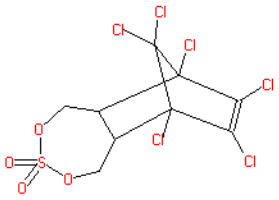
Finding a ‘good’ tea matrix blank - Analysis of Organic Tea Samples

Pesticide Residues in 4 Organic Tea Extracts by GC-MS/MS

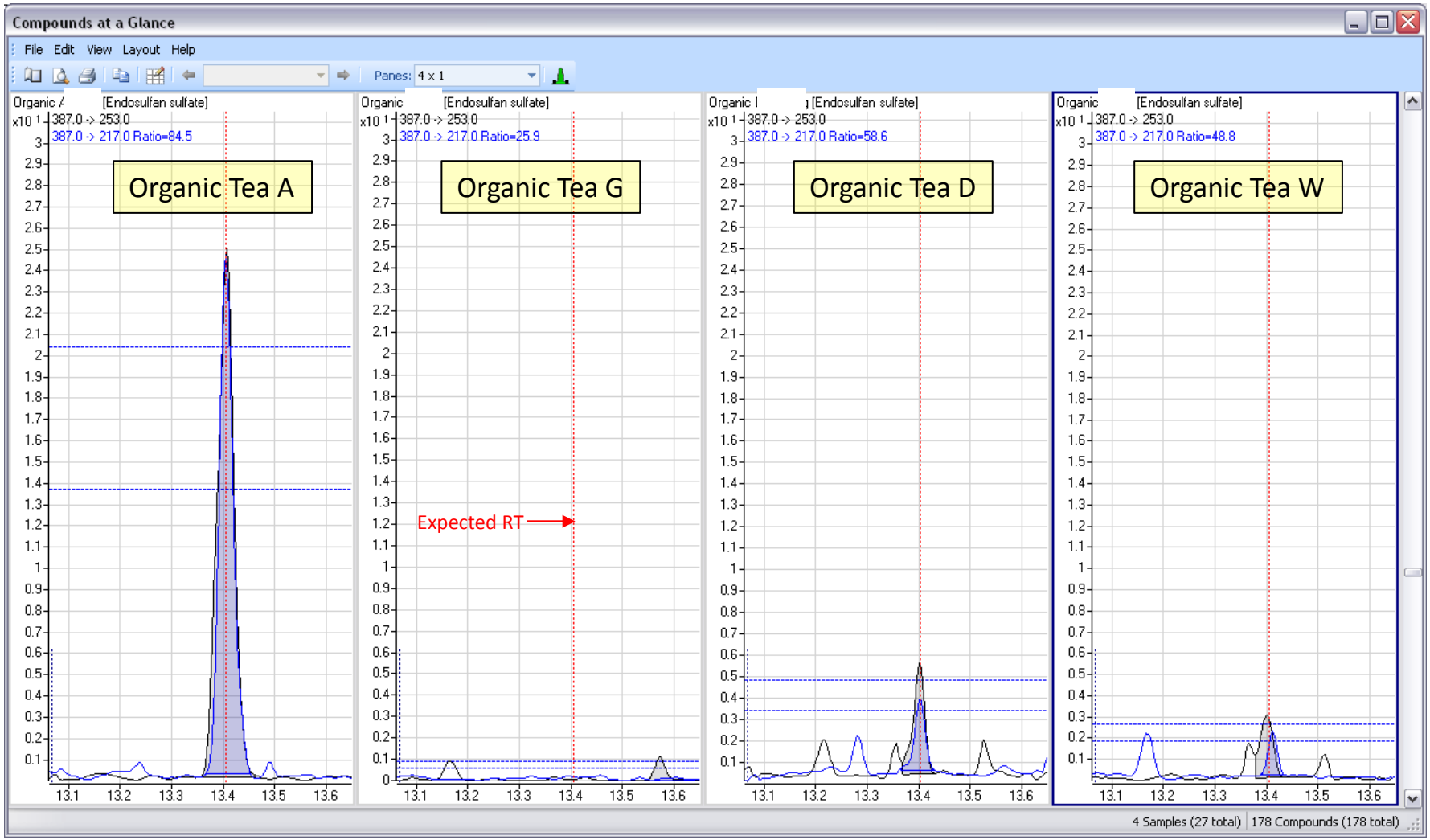
Analyte	Ret Time (min)	Organic A	Organic G	Organic D	Organic W
		ppb	ppb	ppb	ppb
Biphenyl	3.55	0.33	0.67	0.24	0.41
o-Phenyl phenol	4.42	0.25	0.45	0.24	0.24
a-Endosulfan	11.32	0.89			
p,p'-DDE	12.02	0.18			
b-Endosulfan	12.59	1.15			
Endosulfan sulfate	13.40	3.31		0.60	
pp'-DDT	13.51	0.45		0.27	

Σ Endosulfans = 5.35 ppb, Equivalent to 0.027 mg/kg
EU MRL (Tea) = 30 mg/kg





Endosulfan Sulfate Transitions in 4 Organic Tea Extracts

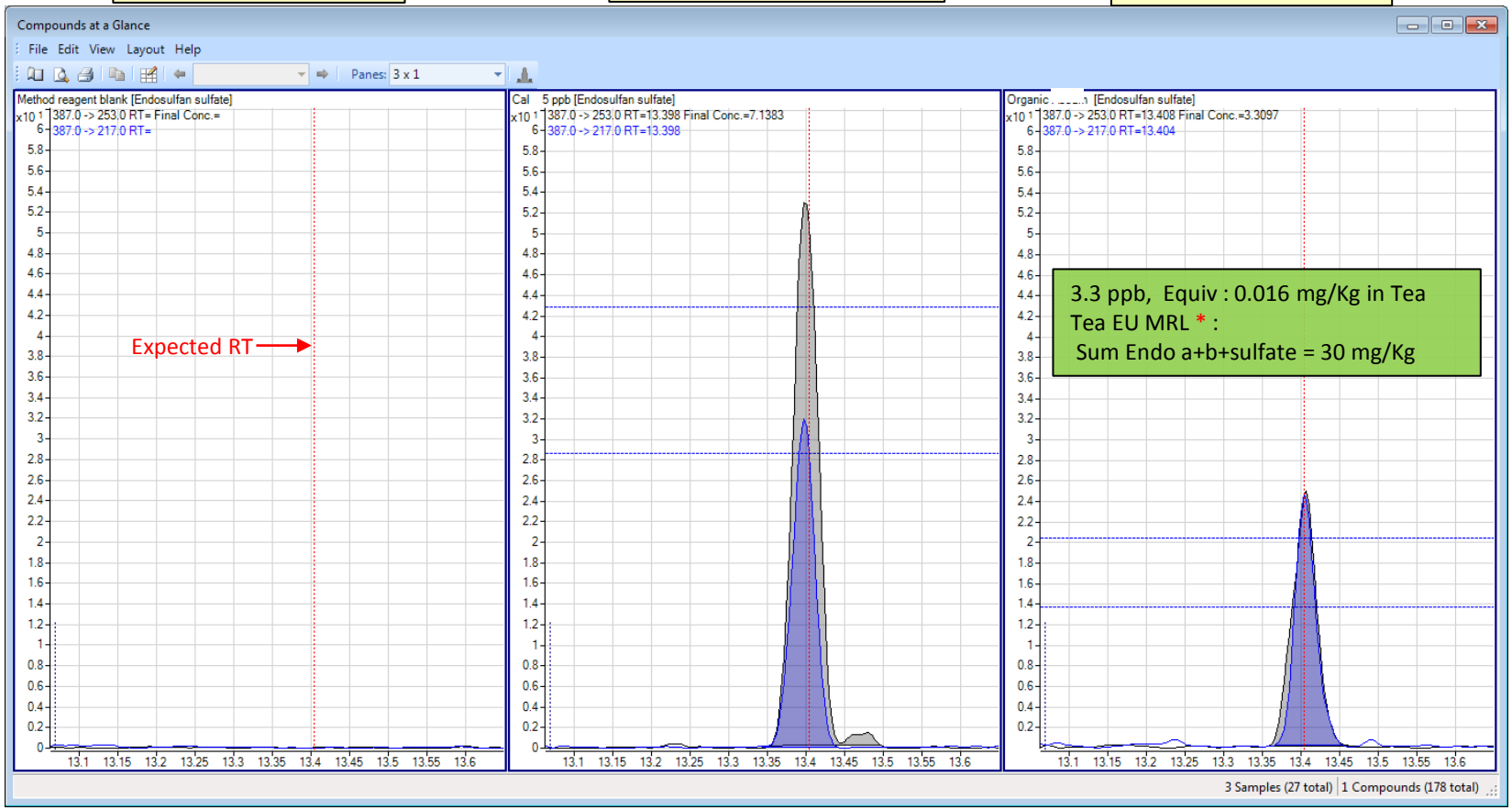


Endosulfan Sulfate (?) in Organic Tea Extract – Using 1 Qualifier Transition

Reagent blank

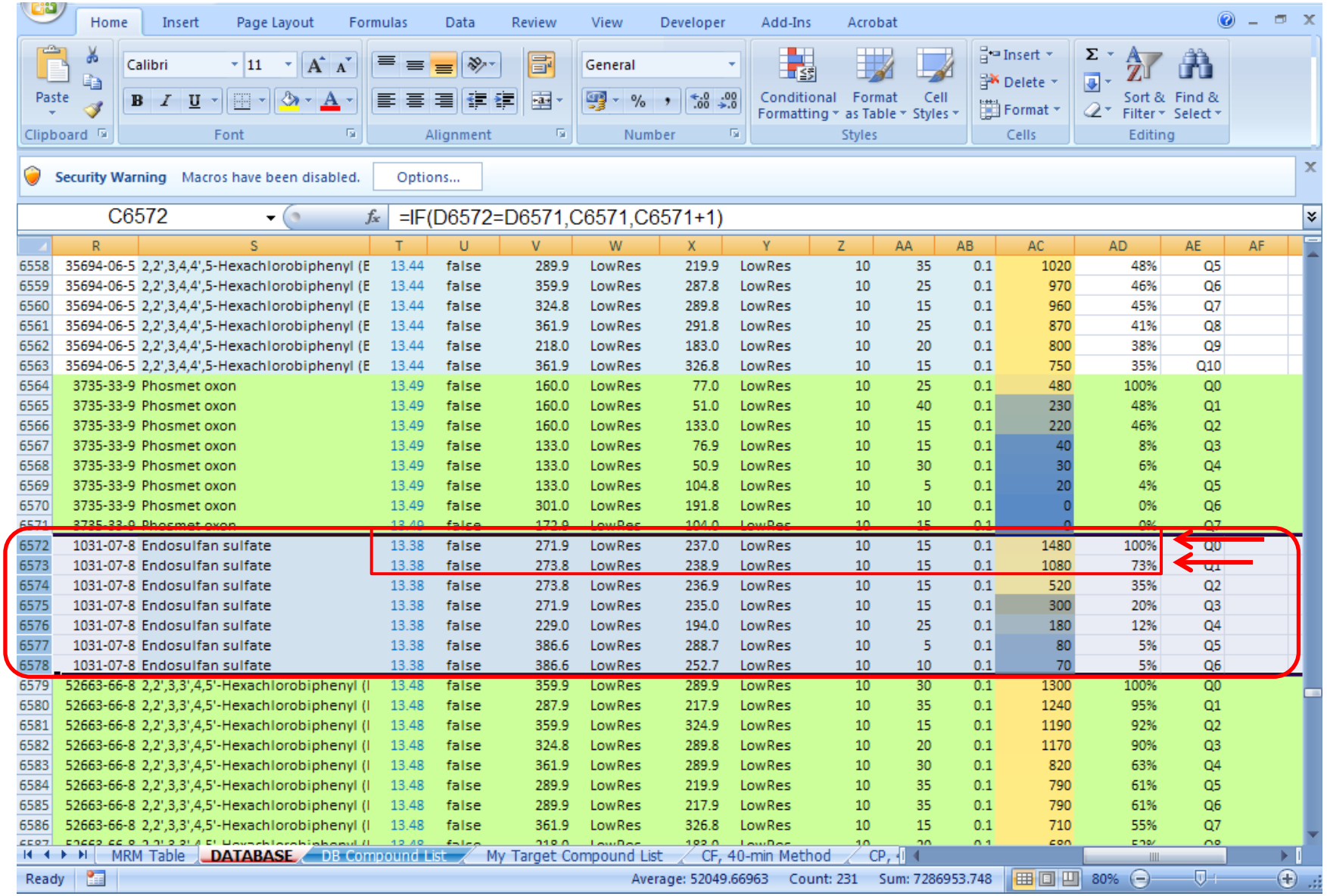
Matrix Matched Std 5 ppb

Organic Tea A



* Regulation (EC) No 396/2005, Tea (dried leaves and stalks, fermented or otherwise, of Camellia sinensis)

Optimized Endosulfan Sulfate MRM Transitions in the G9250AA Database



Security Warning Macros have been disabled. Options...

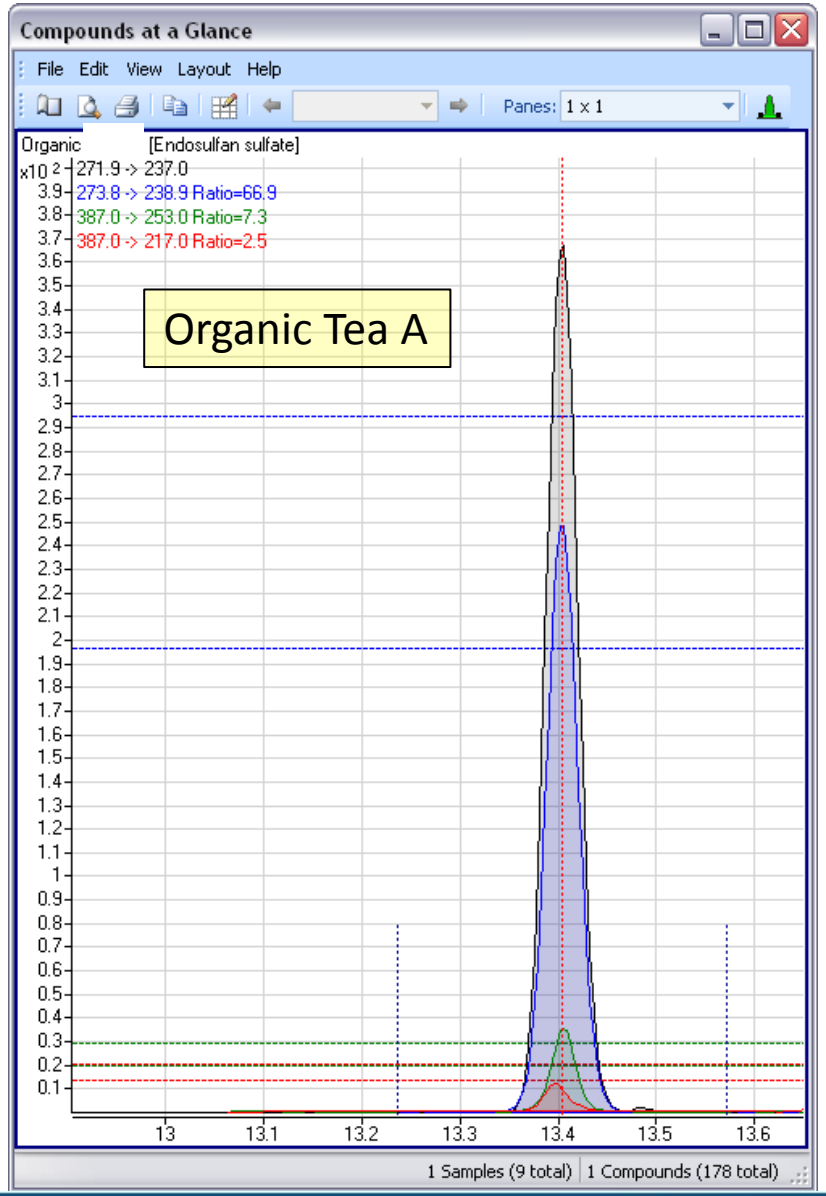
C6572 =IF(D6572=D6571,C6571,C6571+1)

	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF
6558	35694-06-5	2,2',3,4,4',5-Hexachlorobiphenyl (E	13.44	false	289.9	LowRes	219.9	LowRes	10	35	0.1	1020	48%	Q5	
6559	35694-06-5	2,2',3,4,4',5-Hexachlorobiphenyl (E	13.44	false	359.9	LowRes	287.8	LowRes	10	25	0.1	970	46%	Q6	
6560	35694-06-5	2,2',3,4,4',5-Hexachlorobiphenyl (E	13.44	false	324.8	LowRes	289.8	LowRes	10	15	0.1	960	45%	Q7	
6561	35694-06-5	2,2',3,4,4',5-Hexachlorobiphenyl (E	13.44	false	361.9	LowRes	291.8	LowRes	10	25	0.1	870	41%	Q8	
6562	35694-06-5	2,2',3,4,4',5-Hexachlorobiphenyl (E	13.44	false	218.0	LowRes	183.0	LowRes	10	20	0.1	800	38%	Q9	
6563	35694-06-5	2,2',3,4,4',5-Hexachlorobiphenyl (E	13.44	false	361.9	LowRes	326.8	LowRes	10	15	0.1	750	35%	Q10	
6564	3735-33-9	Phosmet oxon	13.49	false	160.0	LowRes	77.0	LowRes	10	25	0.1	480	100%	Q0	
6565	3735-33-9	Phosmet oxon	13.49	false	160.0	LowRes	51.0	LowRes	10	40	0.1	230	48%	Q1	
6566	3735-33-9	Phosmet oxon	13.49	false	160.0	LowRes	133.0	LowRes	10	15	0.1	220	46%	Q2	
6567	3735-33-9	Phosmet oxon	13.49	false	133.0	LowRes	76.9	LowRes	10	15	0.1	40	8%	Q3	
6568	3735-33-9	Phosmet oxon	13.49	false	133.0	LowRes	50.9	LowRes	10	30	0.1	30	6%	Q4	
6569	3735-33-9	Phosmet oxon	13.49	false	133.0	LowRes	104.8	LowRes	10	5	0.1	20	4%	Q5	
6570	3735-33-9	Phosmet oxon	13.49	false	301.0	LowRes	191.8	LowRes	10	10	0.1	0	0%	Q6	
6571	3735-33-9	Phosmet oxon	13.49	false	172.9	LowRes	104.0	LowRes	10	15	0.1	0	0%	Q7	
6572	1031-07-8	Endosulfan sulfate	13.38	false	271.9	LowRes	237.0	LowRes	10	15	0.1	1480	100%	Q0	
6573	1031-07-8	Endosulfan sulfate	13.38	false	273.8	LowRes	238.9	LowRes	10	15	0.1	1080	73%	Q1	
6574	1031-07-8	Endosulfan sulfate	13.38	false	273.8	LowRes	236.9	LowRes	10	15	0.1	520	35%	Q2	
6575	1031-07-8	Endosulfan sulfate	13.38	false	271.9	LowRes	235.0	LowRes	10	15	0.1	300	20%	Q3	
6576	1031-07-8	Endosulfan sulfate	13.38	false	229.0	LowRes	194.0	LowRes	10	25	0.1	180	12%	Q4	
6577	1031-07-8	Endosulfan sulfate	13.38	false	386.6	LowRes	288.7	LowRes	10	5	0.1	80	5%	Q5	
6578	1031-07-8	Endosulfan sulfate	13.38	false	386.6	LowRes	252.7	LowRes	10	10	0.1	70	5%	Q6	
6579	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	359.9	LowRes	289.9	LowRes	10	30	0.1	1300	100%	Q0	
6580	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	287.9	LowRes	217.9	LowRes	10	35	0.1	1240	95%	Q1	
6581	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	359.9	LowRes	324.9	LowRes	10	15	0.1	1190	92%	Q2	
6582	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	324.8	LowRes	289.8	LowRes	10	20	0.1	1170	90%	Q3	
6583	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	361.9	LowRes	289.9	LowRes	10	30	0.1	820	63%	Q4	
6584	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	289.9	LowRes	219.9	LowRes	10	35	0.1	790	61%	Q5	
6585	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	289.9	LowRes	217.9	LowRes	10	35	0.1	790	61%	Q6	
6586	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	361.9	LowRes	326.8	LowRes	10	15	0.1	710	55%	Q7	
6587	52663-66-8	2,2',3,3',4,5'-Hexachlorobiphenyl (I	13.48	false	218.0	LowRes	183.0	LowRes	10	20	0.1	680	53%	Q8	

MRM Table | DATABASE | DB Compound List | My Target Compound List | CF, 40-min Method | CP,

Ready Average: 52049.66963 Count: 231 Sum: 7286953.748 80%

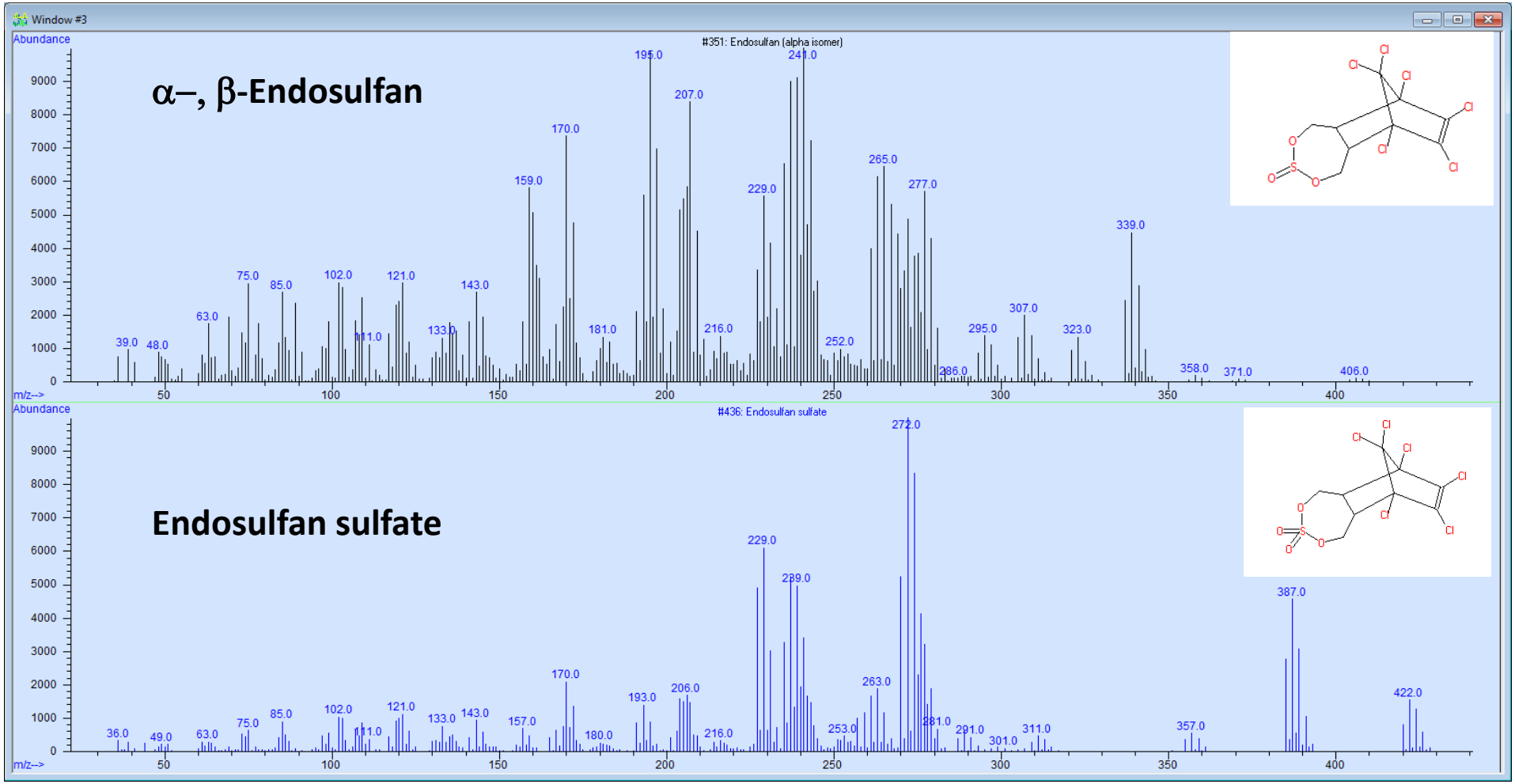
Endosulfan Sulfate (✓) in Organic Tea Extract – Using 3 Qualifier Transitions



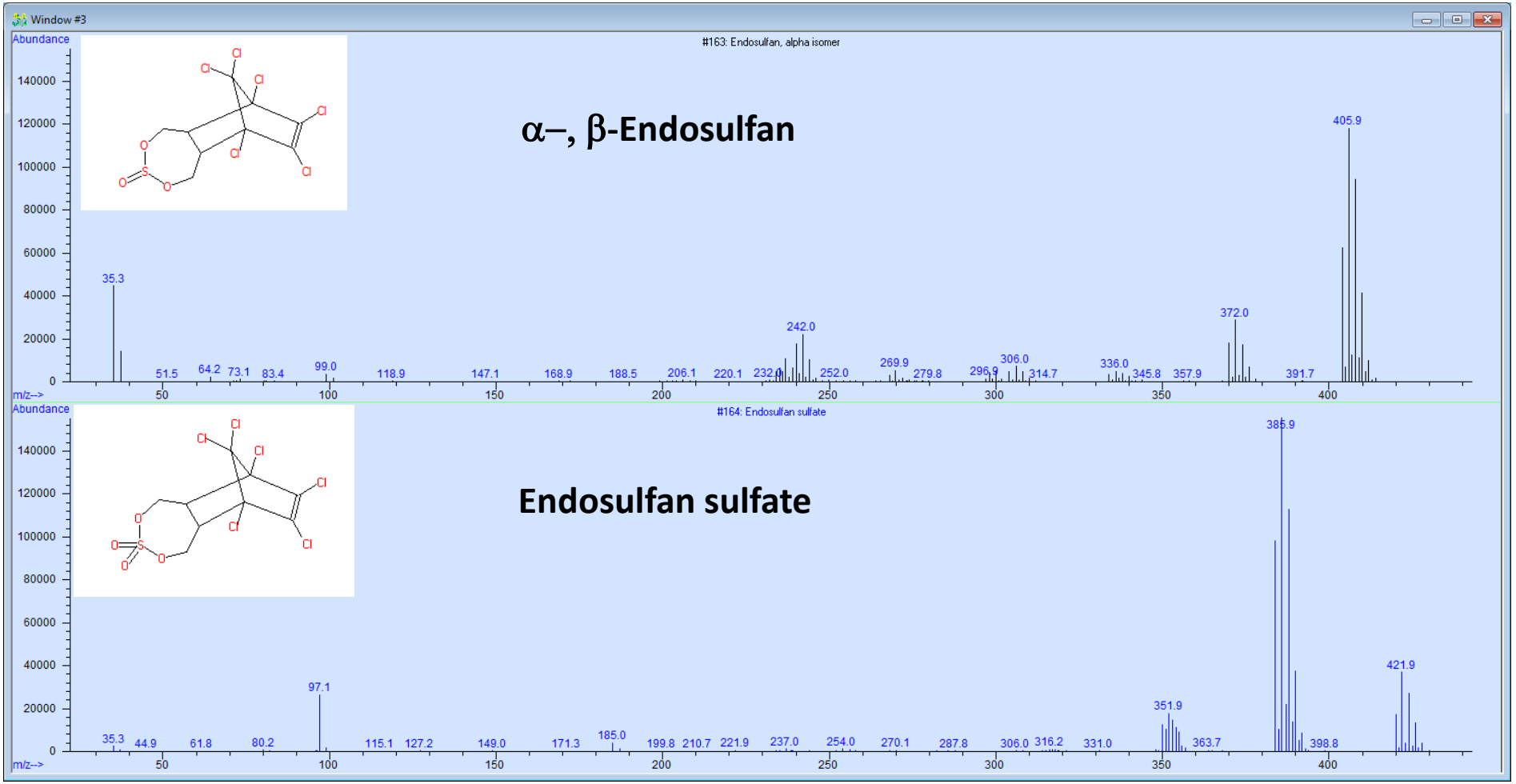
… demonstrates the value of immediate access to multiple optimized transitions in the G9250AA MRM Database

-Not just to avoid matrix interferences but also for additional confirmation

Endosulfan α, β and Sulfate - 5975 EI Mode

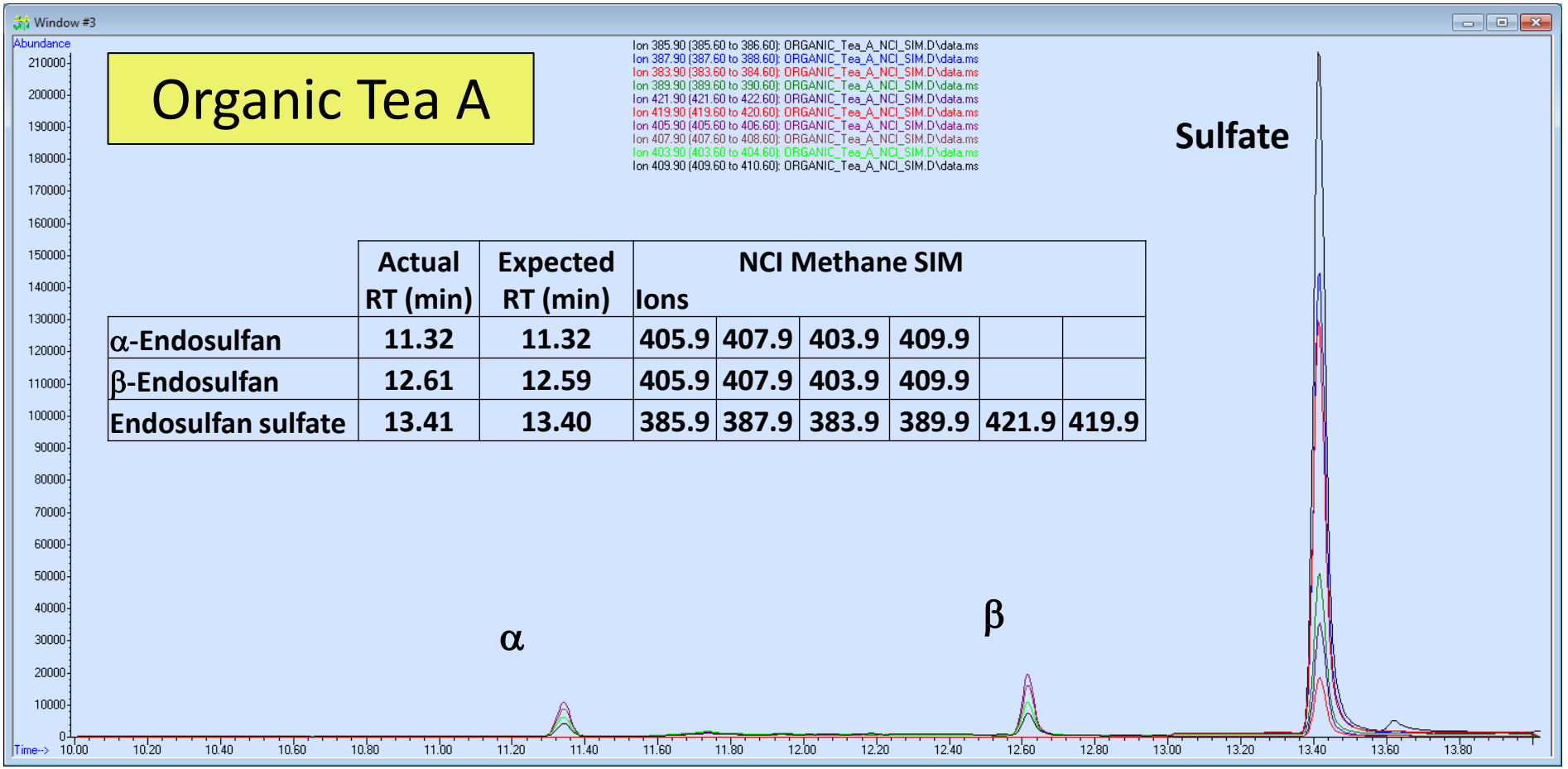


Endosulfan α, β and Sulfate -
5975 NCI Methane Mode



Endosulfan α, β and Sulfate (✓) in Organic Tea Extract A

5975 NCI Methane SIM



	Actual RT (min)	Expected RT (min)	NCI Methane SIM Ions					
α-Endosulfan	11.32	11.32	405.9	407.9	403.9	409.9		
β-Endosulfan	12.61	12.59	405.9	407.9	403.9	409.9		
Endosulfan sulfate	13.41	13.40	385.9	387.9	383.9	389.9	421.9	419.9

Updated website

http://www.chem.agilent.com/en-US/Products/Instruments/ms/pages/pesticide_triplequad_gcms_ws.aspx

Summary

- **Pesticide GC/MS/MS Analyzers include**
  - All required hardware / software / application specific consumables
  - Retention time locked methods for ease of method set-up / adding targets
  - Back-flush for robust chromatography / reduced system maintenance
  - 3 (+1) Pre-configured methods to optimize productivity and / or analyte coverage

- **Pesticides / Environmental Pollutants MRM Database**
  - Over 1000 analytes, Over 8000 transitions and Locked RTs
  - Build custom GC-MS/MS MRM methods in minutes

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7000B QQQ

Additional Slides
(not shown at EPRW 2012)

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Outline of *QuickStart* GC-MS/MS method

Sample extracts are injected into a CO_2 cooled Multi-mode Inlet (MMI) using either cold splitless injection or solvent vent (large volume) injection. The analytical column is a 15m x 0.25mm ID x 0.25um HP-5MSUI column, operated in constant pressure mode. The method is retention time locked and the operating pressure is set to give a retention time for Trifluralin herbicide of 5.819 minutes. This will give rise to analyte retention times precisely scaled to be 2x faster than the standard Agilent RTL pesticide method which employs a 30m x 0.25m m ID x 0.25um HP-5MSUI column.

These locked retention times considerably reduce the time required to create multi-residue MRM methods and software tools exist to create MRM methods with optimized conditions for quantitative analysis. Agilent has a database of locked retention times, pre-cursor and product ions and the associated collision energies for more than 1000 GC-amenable pesticides, EDCs and Pollutants.

The outlet of the 15m column is connected to an Agilent capillary flow device (a pressure controlled tee, PCT) mounted inside the GC oven, held at a constant pressure setting provided by a pneumatics control module (PCM). The outlet of the PCT is connected to the QQQ interface using a 0.50m x 0.15mm ID x 0.15um DB5-MSUI restrictor.

This configuration (with the PCT at the outlet end of the analytical column) is referred to as a post-column back flush configuration. Once the final analyte of interest has eluted in to the mass spectrometer, the system goes in to post-run mode for a few minutes. During post-run, the inlet pressure to the 15m column is dropped and the pressure at the PCT increased. This creates a reverse flow (back flush) of carrier gas and sweeps any non-eluted higher-boiling components remaining in the column out through the split vent.

After post-run and prior to the next injection, inlet and PCT pressure set-points are reset to their starting values.

The use of back flush provides :

- Consistent analyte retention times
- Robust chromatography and consistent analyte chromatographic peak shapes
- Prevention of high boiling matrix from contaminating the MS ion source
- Extended column life-time and reduced cycle times by removing the need for high-temperature bake-out between runs

GC-QQQ Analysis Conditions (2x RTL Pesticide Method)

Gas Chromatograph	Agilent 7890A
Columns	(1) 15.0m x 0.25mm ID x 0.25 um HP-5MS Ultra Inert (19091S-431SI) Inlet CO2 cooled Multimode Inlet, outlet Pressure controlled tee (2) 0.50m x 0.15mm ID x 0.15um DB-5MSUI (Cut from 165-6626) Inlet Pressure controlled tee at 2.0 psig (PCM), outlet Vacuum
Carrier gas	Helium
Carrier gas mode	Constant pressure
Column Head pressure	15.290 psi , Retention Time Locked to Trifluralin at 5.818 mins
Injection Port	CO2 cooled, Multimode Inlet
Auto-sampler	Agilent 7693A
Injection mode	Cold Splitless, Purge delay 1.0 min Purge Flow 50.0 ml/min at 1.0 min
MMI Temperature Program	80 (0.1) – 600 deg C/min – 300 deg C
Injection volume	1.0 µL
Injection port liner	Multi-baffle 4mm , deactivated (5190-2296)
Oven program deg C (min)	70 (1) – 50 deg C /min – 150 (0) 6 – 200 (0) - 16 -280 (4.07) deg C (Run time = 20.0 mins)
Mass Spectrometer	Agilent 7000B QQQ
MS Interface	280 deg C
MS Source	280 deg C
MS Quad 1	150 deg C
MS Quad 2	150 deg C
Backflush conditions	Post run, 3 mins, Oven 280 deg C, PCM 60 psig, Inlet 1 psig
Detection mode	MRM, 2 Transitions per analyte, Transitions 20ms or 10 ms dwell times
EI Tune	Atune, Gain normalized, G = 10

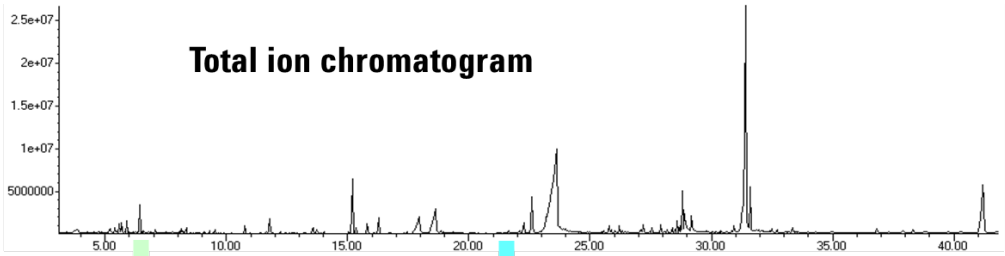
GC-QQQ acquiring data in MRM mode is *ipso facto* a target based analysis

- *You can only find / quantify what you are looking for…*

Could there be other pesticide residues present in the samples? …

… Let's find out by using the 5975 MSD and Deconvolution Reporting Software !

GC-MSD DRS Results – Green Bean & Mint Extracts



Targets are identified by comparison to locked R.T.s and 3 qualifier ion ratios, then quantified using target ion area vs ISTD cal table

AMDIS 32 deconvolutes component spectra and searches target MS database using locked RT used as a qualifier

Deconvoluted Target spectra confirmed by AMDIS, searched against NIST11 MS database

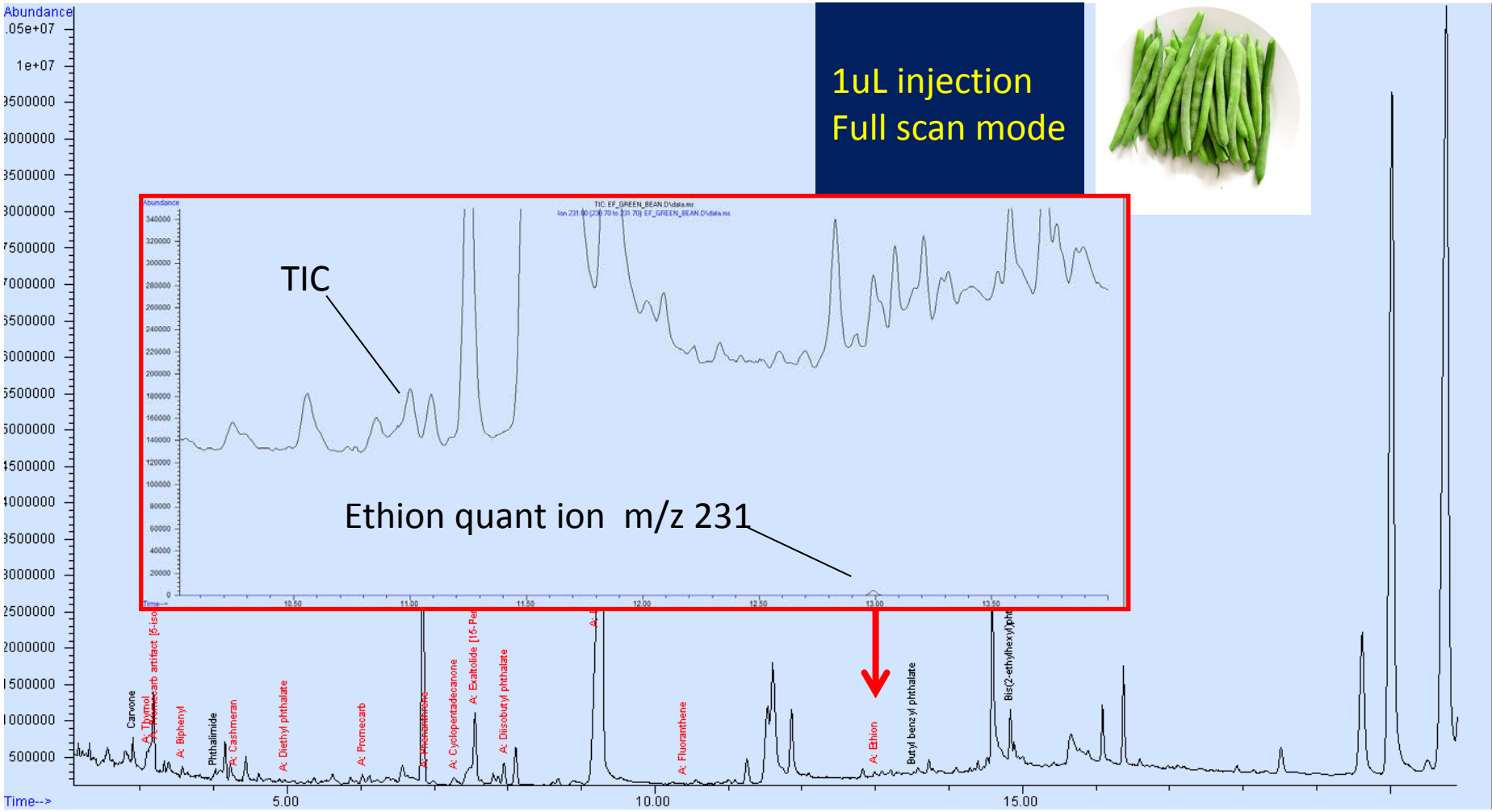
Confirmed AMDIS hits

Confirmed NIST11 hits

Quant Results

Combined quantitative and qualitative HTML Summary report

‘QuickStart’ Method 5975 MSD – TIC Green Bean Extract



Black peak labels = targets confirmed by 4 EICs in Chemstation

Red peak labels = targets confirmed by DRS (AMDIS)

MSD Deconvolution Report
Sample Name: x2 RTL method
Data File: C:\DOCUME~1\csandy\MYDOCU~1\EUROFI~1\EU1BB5~1\EF_GRE~1.D
Date/Time: 10:47 AM Tuesday, Oct 25 2011

Adjacent Peak Subtraction = 1
Resolution = Medium
Sensitivity = High

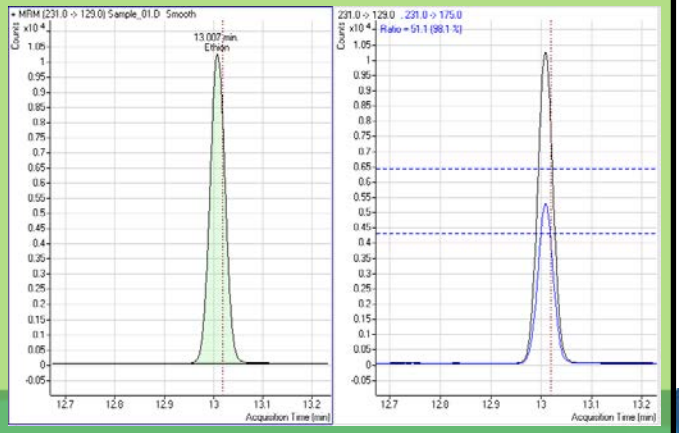
Shape Requirements = Medium

The NIST library was searched for the components that were found in the AMDIS target library.

DRS GC-MS Results 'QuickStart' Method Green Bean Extract

			Amount (ng)		AMDIS		NIST	
R.T.	Cas #	Compound Name	Chem station	AMDIS	Match	R.T. Diff sec.	Reverse Match	Hit Num.
2.9016	99490	Carvone	0.84	0.76	94	-1.1	94	1
3.081	89838	Thymol		0.05	47	2.3		
3.0812	95452087	Cyclohexane, 2-ethenyl-1,1-dimethyl-3-methylene-					77	1
3.205	3228033	Promecarb artifact [5-isopropyl-3-methy		0.07	74	4.1		
3.2053	1450722	Ethanone, 1-(2-hydroxy-5-methylphenyl)-					82	1
3.562	92524	Biphenyl		0.05	87	1.3	81	3
3.9869	85416	Phthalimide	0.01	0.02	55	-0.3	65	3
4.2836	33704619	Cashmeran		0.1	75	-3.1	71	25
4.9749	84662	Diethyl phthalate		0.04	86	-0.4	82	1
6.029	2631370	Promecarb		0.79	50	8.4		
6.0293	0000	p-Anisic acid, 4-nitrophenyl ester					92	1
6.8441	1517222	Phenanthrene-d10			99	-2.3	88	2
6.8919	85018	Phenanthrene		0.03	52	-2.3	76	7
7.267	502727	Cyclopentadecanone		0.16	49	-3.7		
7.2673	34450185	17-Octadecynoic acid					81	1
7.5459	106025	Exaltolide [15-Pentadecanolide]		1.13	67	-1.1		
7.5459	102608537	3,7,11,15-Tetramethyl-2-hexadecen-1-ol					92	1
7.9487	84695	Diisobutyl phthalate		2.88	97	0.1	89	3
9.183	84742	Di-n-butylphthalate		0.2	86	-3.0	87	7
10.390	206440	Fluoranthene			47	-3.6		
10.3903	28816946	Pyrene, 10b,10c-dihydro-10b,10c-dipropyl-, trans-					58	1
12.993	563122	Ethion		0.03	79	-1.0	78	1
13.4935	85687	Butyl benzyl phthalate	0.03		66	1.3	74	1
14.8317	117817	Bis(2-ethylhexyl)phthalate	1.96	1.86	95	0.9	78	8
6.846		Phenanthrene-d10	10					

QQQ Ethion RT = 13.007 minutes
Delta RT = 0.84 seconds !!!



DRS GC-MS Results
‘QuickStart’ Method Green Bean Extract

Full Scan 5975 MSD-DRS Confirmed : Ethion

GC-QQQ Confirmed : Ethion at 25 ppb

No other pesticide residues found

'QuickStart' Pesticide Method DRS Results– Mint Extract

MSD Deconvolution Report
Sample Name: x2 RTL method
Data File: C:\msdchem\1\DATA\EUROFI~1\EF_MINT.D
Date/Time: 11:13 AM Tuesday, Nov 23 2010

Adjacent Peak Subtraction = 1
Resolution = Medium
Sensitivity = High
Shape Requirements = Medium

The NIST library was searched for the components that were found in the AMDIS target library.

			Amount (ng)		AMDIS		NIST	
R.T.	Cas #	Compound Name	Chem station	AMDIS	Match	R.T. Diff sec.	Reverse Match	Hit Num.
2.9518	99490	Carvone			99	4.9	94	3
3.0363	3964565	Profenofos metabolite (4-Bromo-2-chlorophenol)			83	9.0	85	2
3.2124	3228033	Promecarb artifact [5-isopropyl-3-methylphenol]			71	4.9		
3.2124	7786610	2-Methoxy-4-vinylphenol					74	1
3.4105	97530	Eugenol	5.5		94	1.6	91	1
6.8488	1517222	Phenanthrene-d10			99	-1.7	87	2
7.5652	106025	Exaltolide [15-Pentadecanolide]			56	1.2		
7.5652	102608537	3,7,11,15-Tetramethyl-2-hexadecen-1-ol					91	1
7.9557	84695	Diisobutyl phthalate			85	1.0	82	17
8.6592	57837191	Metalaxyl			75	-1.2	67	2
9.1908	84742	Di-n-butylphthalate			73	-2.0	73	19
10.0103	10544500	Sulfur (S8)			95	0.2	91	1
13.4684	126833178	Fenhexamid			77	2.8	68	8
13.7604	107534963	Tebuconazole			88	5.3	85	1
14.8428	117817	Bis(2-ethylhexyl)phthalate	1.87		93	2.2	86	3
15.2083	68085858	Cyhalothrin I (lambda)			91	2.7		
15.2083	91465086	.lambda.-Cyhalothrin					88	1
17.796	71561110	Pyrazoxyfen	0.03					
18.0159	52918635	Deltamethrin			63	1.8	69	1
6.851		Phenanthrene-d10	10					

1uL injection
AMDIS Match >55

Biphenyl, Diphenylamine, Iprodione and Boscalid not reported by DRS with 1uL Injection, but are with 5uL injection

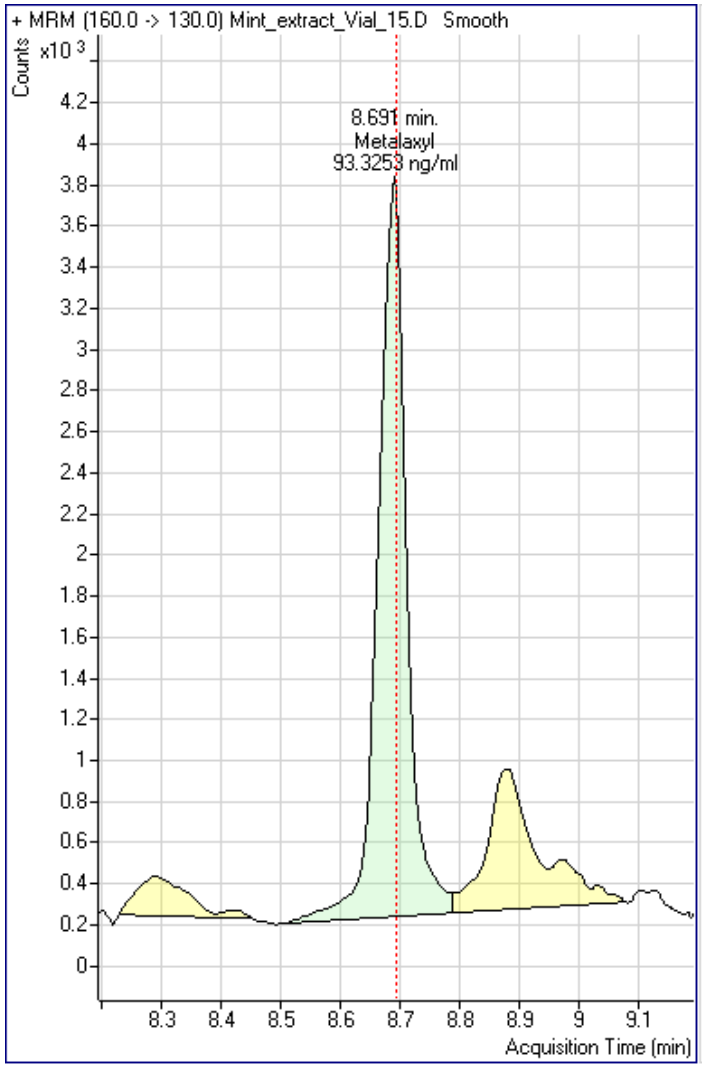
These 2 analytes were not in the original 178 compound MRM method

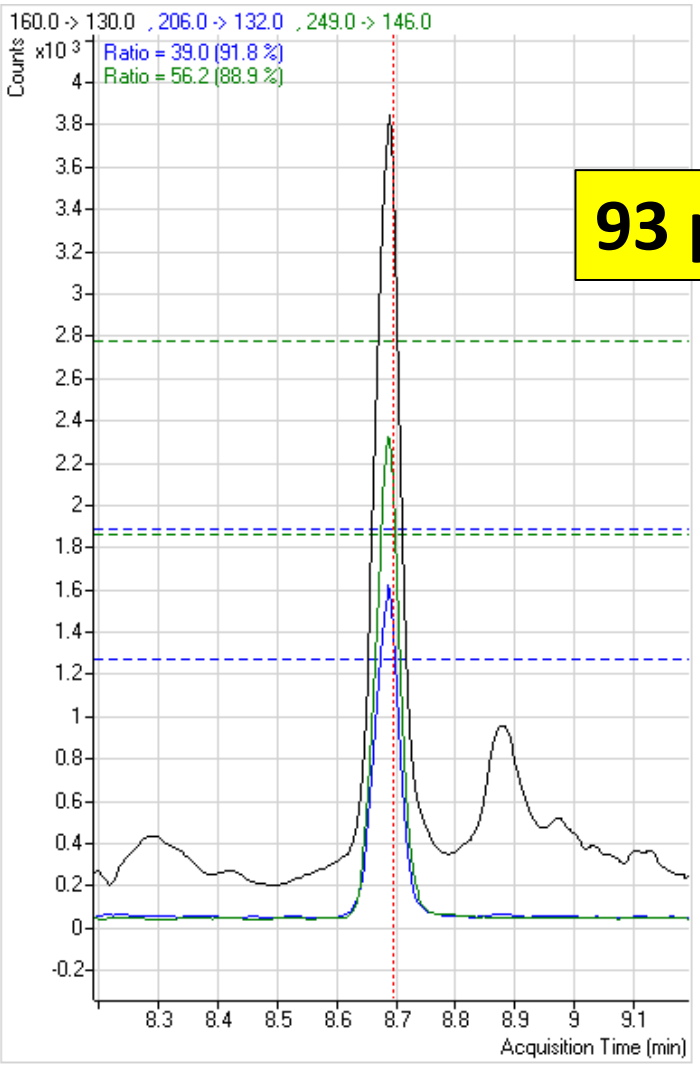
GC-QQQ – 178 (+2) Target Analytes

Dichlorvos	Diazinon	Parathion ethyl	Methidathion	Carbophenothion	Tebufenpyrad
Dichlobenil	Phosphamidon I	Isobenzan	Bromophos-ethyl	Endosulfan sulfate	Fenazaquin
Biphenyl	BHC delta isomer	Chlorthal-dimethyl	Endosulfan (alpha isomer)	Quinoxyfen	Bifenox
Mevinphos	Paraoxon-methyl	Fenson	Pyrifenox II	Cyanofenphos	Tetradifon
Propham	Terbacil	Nitrothal-isopropyl	Chlordane, cis-	Fenhexamid	Phenothrin I
Methacrifos	Tefluthrin, cis-	Tetraconazole	Disulfoton sulfone	Propiconazole-II	Phenothrin II
Phenylphenol, o-	Etrimfos	Isodrin	Tetrachlorvinphos	DDT, o,p'-	Furathiocarb
Tecnazene	Chlorothalonil	Butralin	Paclobutrazol	DDT, p,p'-	Phosalone
Propachlor	Formothion	Pirimiphos-ethyl	Chlorfenson	Lenacil	Leptophos
Propoxur	Dichlofenthion	Cyprodinil	Hexaconazole	Propiconazole-I	Cyhalothrin I (lambda)
Diphenylamine	Metribuzin	Heptachlor epoxide	Prothiofos	Hexazinone	Benfuracarb
Demeton-S- methyl	Chlorpyrifos Methyl	Heptachlor exo-epoxide isomer B	Dieldrin	Nuarimol	Pyrazophos
Chlorpropham	Parathion methyl	Metazachlor	Profenofos	Tebuconazole	Acrinathrin
Dioxabenzofos	Spiroxamine I	Pendimethalin	DDE, p,p'-	Propargite	Dialifos
Benfluralin	Spiroxamine II	Penconazole	Fludioxonil	Piperonyl butoxide	Bitertanol I
Trifluralin	Vinclozolin	Tolylfluanid	Imazalil	Resmethrin I	Bitertanol II
Phorate	Heptachlor	Captan	Myclobutanil	Resmethrin II	Spirodiclofen
BHC alpha isomer	Tolclofos-methyl	Pyrifenox I	Endrin	Iprodione	Permethrin I
Hexachlorobenzene	Carbaryl	Chlozolinate	Kresoxim-methyl	Phosmet	Pyridaben
Dicloran	Paraoxon	Folpet	Cyproconazole	Pyridaphenthion	Permethrin II
Ethoxyquin	Metalaxyl	Isofenphos	Endosulfan (beta isomer)	Tetramethrin I	Prochloraz
BHC beta isomer	Prosulfocarb	Chlorfenvinphos	Chlorfenapyr	Bromopropylate	Cyfluthrin I-IV
Lindane	Fenitrothion	Quinalphos	Chlorobenzilate	EPN	Boscalid
Quintozene	Dichlofluanid	Fluazinam	Chlordecone	Fenoxycarb	Cypermethrin I-IV
Isocarbamide		Phenthoate	DDD, p,p'-	Carbosulfan	Fenvalerate I
Terbufos	Aldrin	Mecarbam	Oxadixyl	Dicofol, p,p'-	Fenvalerate II
Fonofos	Fenthion	Fipronil	Ethion	Bifenthrin	Fluvalinate-tau-I
Propetamphos	Diethofencarb	Furalaxyl	Tetrasul	Tetramethrin II	Indoxacarb
Propyzamide	Chlorthion	Procymidone	Mepronil	Methoxychlor	Deltamethrin
Pyrimethanil	Chlorpyrifos	Chlordane, trans-	Ofurace	Fenpropathrin	Famoxadone

Analytes in red added after DRS analysis

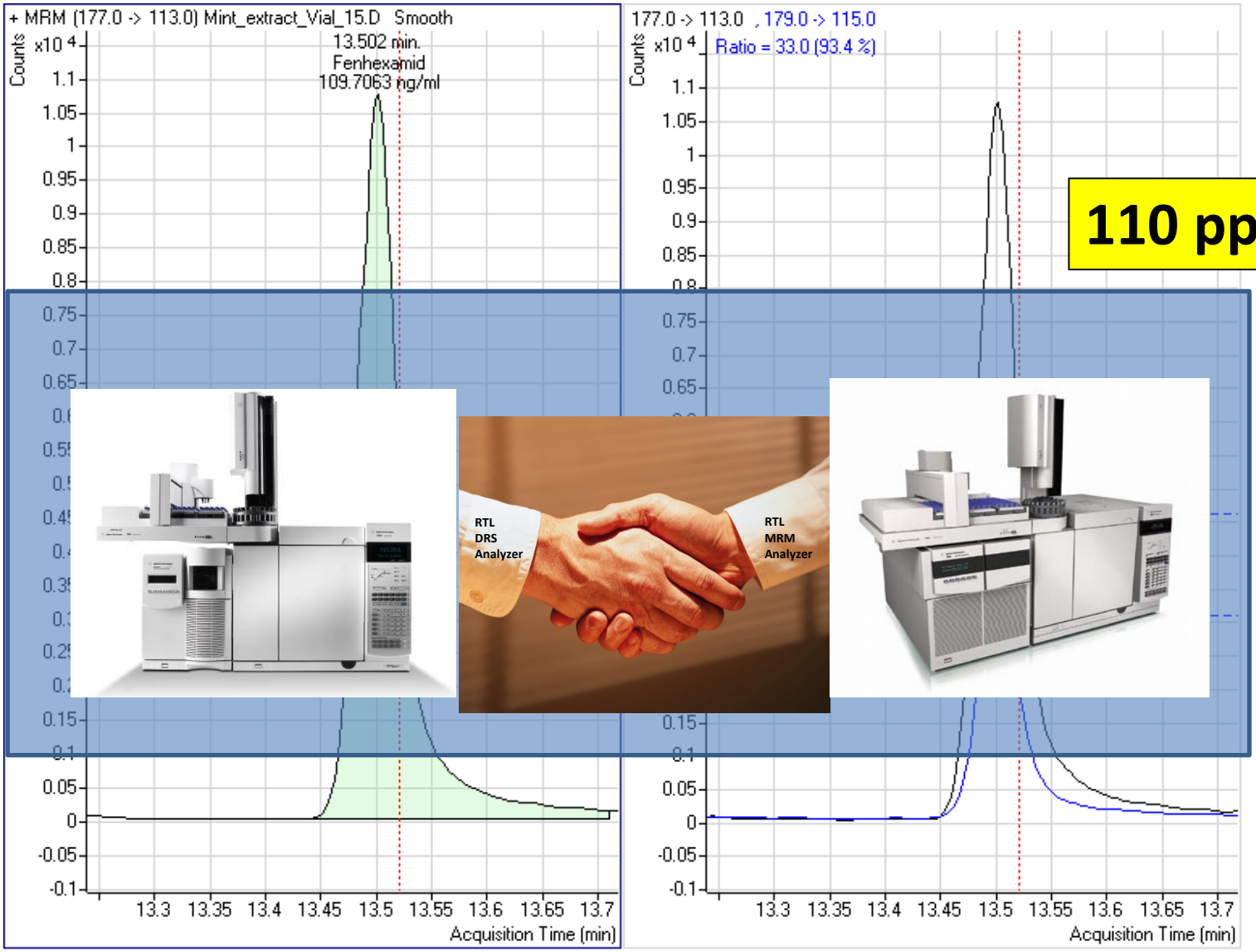
GC-QQQ Quant Result – Metalaxyl – Mint Extract





93 ppb

GC-QQQ Quant Result – Fenhexamid – Mint Extract



110 ppb